

Photooxidation of Petroleum

Mark Bobra
Consultchem
Ottawa, Ontario

E.J. Tennyson
Minerals Management Services
Reston, Virginia

INTRODUCTION

Of all the weathering processes that act upon oil spilled in the environment, photolysis has been one of the least studied. In the environment, the weathering processes occur simultaneously, and differentiating the effects induced by photolysis from changes caused by the other processes can be difficult. Studying the role of photolysis is further complicated by the complex composition of petroleum which means a multitude of photo-induced reactions could conceivably take place, producing an array of photochemical products. Among the photooxidation products that have been identified in previous studies are carbon dioxide, organic acids, carbonyl compounds, hydroxyl compounds, peroxy compounds and sulfoxides. (Freearde et al. (1971); Hansen (1975); Larson et al. (1978, 1979); Patel et al. (1979); Payne and Phillips (1985); Pengerud et al. (1984); Poston et al. (1988); Sydnese et al. (1985); Tjessem et al. (1983)). Many of these products are more water soluble than their parent compounds and thus, can enhance aquatic toxicity. Photolysis may also lead to polymerization (Daling (1988)). Relatively few studies have examined the changes in physical properties of oil induced by photolysis.

The general purpose of this study was to examine the chemical and physical changes that occur in oils as a result of photooxidation. A variety of crude oils and petroleum products were used to determine how different oils are affected by photolysis, and to examine the importance of photolysis as a weathering process.

The results presented in this paper should be regarded as preliminary information since chemical analysis and identification of photooxidation products using GC/MS techniques has yet to be completed. Final results will be published in the future as an Environment Canada EE-report.

EXPERIMENTAL

Materials

The following oils were used in this study:

Adgo Crude Oil (3.0 % by volume evaporated)
Alberta Sweet Mixed Blend Crude Oil (22.8 % by volume evaporated)
Bent Horn Crude Oil (20.6 % by volume evaporated)
Bunker C Fuel Oil
California (API gravity 15) Crude Oil
California (API gravity 11) Crude Oil
Cold Lake Bitumen
Diesel Fuel Oil
Hibernia Crude Oil (16.0 % by volume evaporated)
Prudhoe Bay Crude Oil (14.6 % by volume evaporated)

Oils that are designated as being evaporated were air stripped at room temperature prior to the experiments. The water used in this study was passed through a Millipore purification unit (reverse osmosis, activated carbon and ion-exchange). Bio-crystal marine-mix was added to the water to produce a synthetic sea water of 33 ‰ salinity and 0.02% by weight mercuric chloride was added as an antiseptic. The water was filtered through a 0.2 µm Millipore filter prior to use.

Photolysis

Exposure vessels consisted of 190 mm diameter X 100 mm high, Pyrex crystallizing dishes filled with 2100 mL of water. 26.9 mL of oil was layered upon the water resulting in an initial oil film with an average thickness of 1 mm. The vessel was covered with a 6 mm thick quartz plate which was positioned 8 mm above the rim of the crystallizing dish. The gap between the rim of the dish and the quartz plate was left open to allow normal air flow over the oil surface. A narrow stainless steel tube was inserted into the water layer and held in position so that water could be added to the system without disturbing the oil film if evaporation caused a decrease in the water level. For each oil sample that was exposed to photolysis, a duplicate sample was simultaneously subjected to the same conditions except in a vessel that was completely opaque to light. These samples which were shielded from irradiation were termed "dark controls". The water layer was stirred daily for 90 seconds by a 25 mm egg-shaped stirring bar at 60 RPM. This mixing speed was not of sufficient energy to cause deformation of the oil/water interface for the fresh oils. Some deformation of the interface and shearing of droplets was noticed during mixing of some samples after irradiation.

Photolyses in sunlight were carried out in an unobstructed location free of any reflections or shadows on a roof in Ottawa, Ontario (latitude: 45° 24'N). Experiments were performed during the months of August to mid-October. Sunlight intensity during exposure was measured using p-nitroacetophenone / pyridine actinometry (Dunlin and Mill (1982)).

Experiments were also conducted under fluorescent UVA-340 40-watt lamps (Q-Panel Company) at 22 ± 2°C. The manufacturer claims that the lamp's emission is an excellent simulation of sunlight from 370 nm down to the solar cut-off of 295 nm. Results from this phase of the study are not reported in this paper.

Analysis

At the termination of each experiment, surface oil was separated from the water phase. The mass of oil remaining on the surface was determined gravimetrically. The water phase was filtered through a 1.0 µm Millipore filter and the mass of "sedimented" oil on the filter was determined. Physical properties were determined for the surface oil samples by the analytical methods listed below:

- | | |
|------------------------|------------------------------|
| - density | ASTM method D4052-81 |
| - viscosity (dynamic) | Brookfield Viscometer |
| - interfacial tensions | ASTM method D971-82 |
| - asphaltene content | hexane insoluble precipitate |

All measurements were determined at 15°C.

The natural dispersibility and chemical dispersibility of selected oils were determined using the Swirling Flask Apparatus described by Fingas (1988) and Enersperse 700 dispersant at an oil-to-dispersant ratio of 25:1.

The oil content of the water phase, after filtering, was monitored using a Horiba OCMA-220 Oil Content Analyzer. The Horiba Analyzer was calibrated using a standard mixture of iso-octane, cetane and benzene. The total carbon content of the water phase was measured using a Xertex-Dohrmann DC-80 Series Carbon Analyzer. The pH of water was also determined.

Water samples were extracted using multiple batch extractions of ethyl acetate as described by Aaberg et al. (1985), and the extracts were then concentrated under vacuum. Concentrated extracts and surface oil samples were fractionated by gel chromatography using lipophilic Sephadex LH-20 dextran gel and mixtures of chloroform, methanol and ethanol as described Barth et al. (1981). This fractionation technique separates compounds according to degree of polarity. Preliminary GC/FID results indicate good separation of compounds. Further characterization and identification of photooxidation products are to be performed using GC/MS and will be published in the future.

Selected water and oil samples were examined at various times during the experiment for the presence of microbial activity. No micro-organisms were detected when the samples were subjected to microscopic examination or when inoculated nutrient mediums were incubated.

RESULTS AND DISCUSSION

Table 1 summarizes some of the physical manifestations that were attributed to photolysis. Water beneath irradiated oils acquired a yellowish hue. The intensity of this hue varied from oil to oil, and increased with exposure time. Water beneath shielded oils exhibited no colour change. As noted in the table, precipitates formed in some of the oils during irradiation and some oils developed a crust-like formation at the air-oil interface. Neither of these phenomena were observed in the shielded oils.

Figures 1 to 4 show the change in density as a function of time for exposed oil samples and for shielded oil samples. All samples display an increase in density with time. Increases in density of the shielded (dark) samples can be attributed to the loss of volatile components due largely to evaporation and to a lesser degree, to dissolution. Except for two of the oils, California 15 crude oil and Diesel fuel, the irradiated samples had greater densities than those which were shielded. Possible explanations of why photolysed oils exhibit greater densities than unphotolyzed oils are probably a combination of effects caused by solar irradiation that include: i. the formation of photooxidation products that are denser than their hydrocarbon parents; ii. the formation of photooxidation products that are easily depleted from the surface oil by evaporation and dissolution; and iii. photolysis enhances evaporation by causing an increase in surface temperature of the oil. The temperatures of oil and water phases were monitored for some oils during the experiment and the maximum recorded difference between exposed and dark samples was 3°C. Possible explanations of why the exposed California 15 crude oil and the exposed Diesel fuel oil were less dense than the unexposed samples are: i. photolysis causes a build up of compounds at the air/oil interface which forms a resistive barrier to evaporation and thereby, reduces volatilization of compounds from the underlying oil; and ii. photo-induced reactions remove dense oil phase compounds. The physical changes noted in several of the oils during irradiation (see Table 1) would provide some support for first theory. Hard crustal material did form on the surface of the California 15 crude oil and the oil beneath this crust was relatively fresh in appearance. No crust formation was observed in the Diesel fuel, but

precipitous matter was observed. This precipitous material collected at the oil-water interface and eventually entered the water phase. It could be postulated that this photo-induced precipitation resulted in the removal of the more dense constituents from the oil.

The density measurements also show that several of the oils attained densities that approached or exceeded that of water. California 15, California 11 and Adgo crude oils, and Cold Lake bitumen, all achieved a density of 1 g/mL or greater during the experiments. If these oils were spilled in a marine environment, it is likely that these oils would submerge. As Figures 2, 3 and 4 demonstrate, exposure to solar radiation accelerates an increase in density in some of these oils. The density results obtained in this experiment for California 15 and California 11 crude oils, Bunker C and Cold Lake bitumen are similar to those obtained by Lee et al. (1989).

The measured viscosities of the oil samples are presented in Table 2. For exposure times of 10 days or less, the irradiated oils had significantly higher viscosities than the shielded samples. For exposure times of 20 days or more, the irradiated oils had viscosities that were approximately equal to or slightly less than those of the shielded samples. Photo-polymerization could result in higher viscosity (Daling and Branvik (1988)). The results indicate that effects of photolysis on viscosity over a short term (approximately 10 days or less) can be significant but over a longer term, the effects of photolysis on viscosity will be insignificant compared to the effects of evaporation.

Table 3 presents the measured oil-seawater interfacial tensions. For each oil, the photolysed sample had a lower interfacial tension relative to the shielded oil. Dramatic reductions in interfacial tensions for the irradiated samples of Diesel, Bent Horn crude oil and Adgo crude oil indicate that photooxidation results in the formation of surface-active products. Daling (1988) demonstrated that these photo-produced surfactants play an important role in the emulsification process.

The asphaltene content of surface oil samples are shown in Table 4. Photolysed samples generally had higher asphaltene contents than shielded samples. This increase in asphaltene content could be due to the formation of macro-molecules by photo-polymerization and/or to a concentration effect caused by the removal of photooxidized components from oil. All oils, both exposed and shielded samples, exhibit a general increase in asphalenes as a function of time, except for Diesel and Bent Horn crude oil. The asphaltene content of Diesel and Bent Horn crude reached a maximum value after 3 days of exposure and then steadily declined with time. This trend is seen in both the exposed and shielded samples.

The natural dispersibilities of the oil samples listed in Table 5 were measured; all of the samples essentially had no natural dispersibility as measured by the Swirling Flask apparatus. Therefore, the photo-produced surfactants present in these oils have no noticeable affect upon natural dispersibility. The chemical dispersibilities of these samples are summarized in Table 5. The effect of photooxidation on chemical dispersibility was extremely dependent upon the oil. The effectiveness of Enersperse 700 on photolysed Diesel, ASMB crude oil and Prudhoe Bay crude oil was approximately half of the value obtained with non-photolysed samples. Photolysis had no significant influence upon the chemical dispersibility of Adgo and Bent Horn crude oils.

Table 1: Observations

Oil	Physical Changes During Irradiation
Diesel	<ul style="list-style-type: none"> - within an hour of irradiation the oil's colour began to change from a brownish yellow to a pale yellow and a precipitate formed at the oil/water interface - within six hours the water had a yellowish colour and became turbid - the colour of both the water and oil phases became more intensely yellow with irradiation
Bent Horn Crude	<ul style="list-style-type: none"> - within two hours an orange precipitate was forming in the oil layer - within two days the water had a yellowish colour and became turbid - the oil became more intensely orange and the water more yellow with irradiation
Adgo Crude	<ul style="list-style-type: none"> - within six hours the oil's colour began to change from a medium brown to a brownish orange - within three days the water had a yellowish colour
California 15 Crude	<ul style="list-style-type: none"> - within three days a "skin" had formed at the air/oil interface - within six days the skin becomes slightly encrusted - amount crustal material present increases with time - crustal material flakes off and sinks - after twenty-one days parts of the oil film are overwashed with water and in these areas some bleaching is present - oil beneath crust appears to be relatively fresh - water phase is only slightly coloured
California 11 Crude	<ul style="list-style-type: none"> - same observations as for California 11 Crude but less crustal material is formed
Cold Lake Bitumen	<ul style="list-style-type: none"> - small amount of crust formed - water phase is only slightly coloured
ASMB Crude	<ul style="list-style-type: none"> - small amount of greyish crust formed - water phase is only slightly coloured
Prudhoe Bay Crude	<ul style="list-style-type: none"> - little physical difference between irradiated oil and shielded oil - water phase is only slightly coloured
Hibernia Crude	<ul style="list-style-type: none"> - little physical difference between irradiated oil and shielded oil - water phase is only slightly coloured
Bunker C	<ul style="list-style-type: none"> - small amount of crust formed - water phase is only slightly coloured

Figure 1: Density versus time

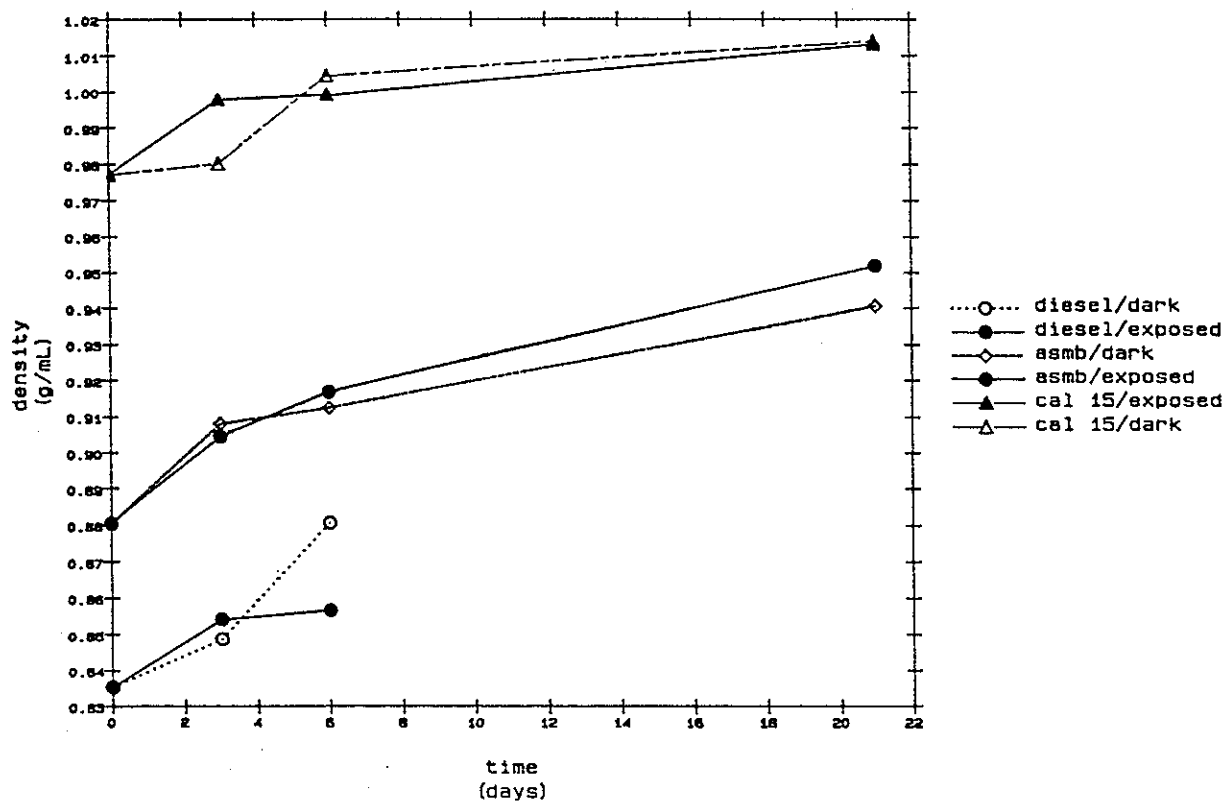


Figure 2: Density versus time

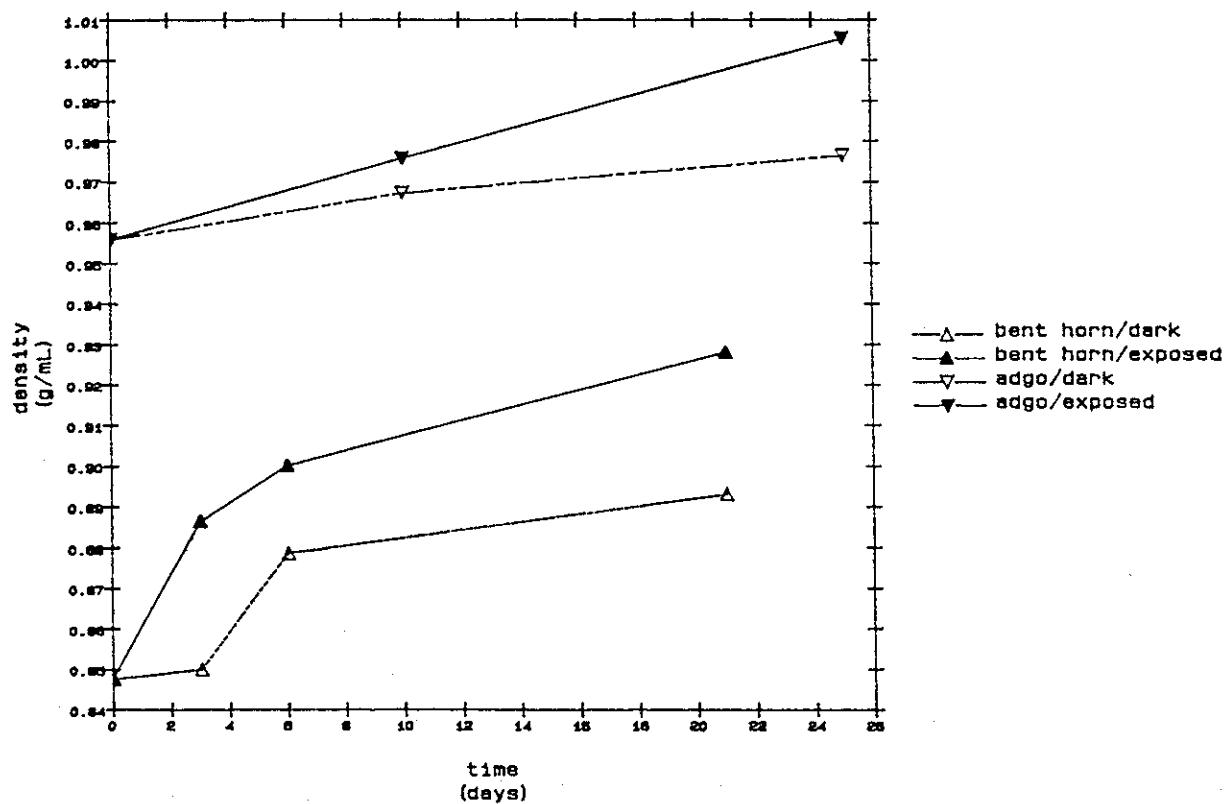


Figure 3: Density versus time

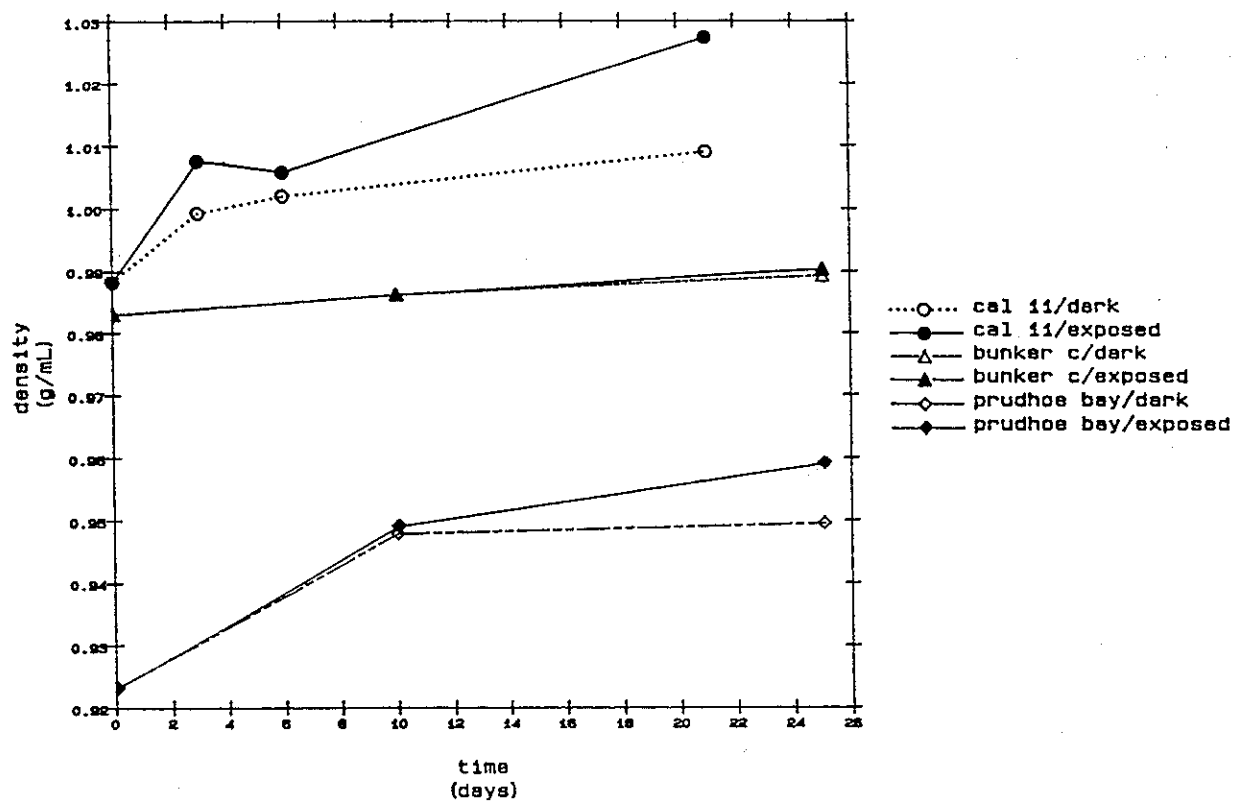
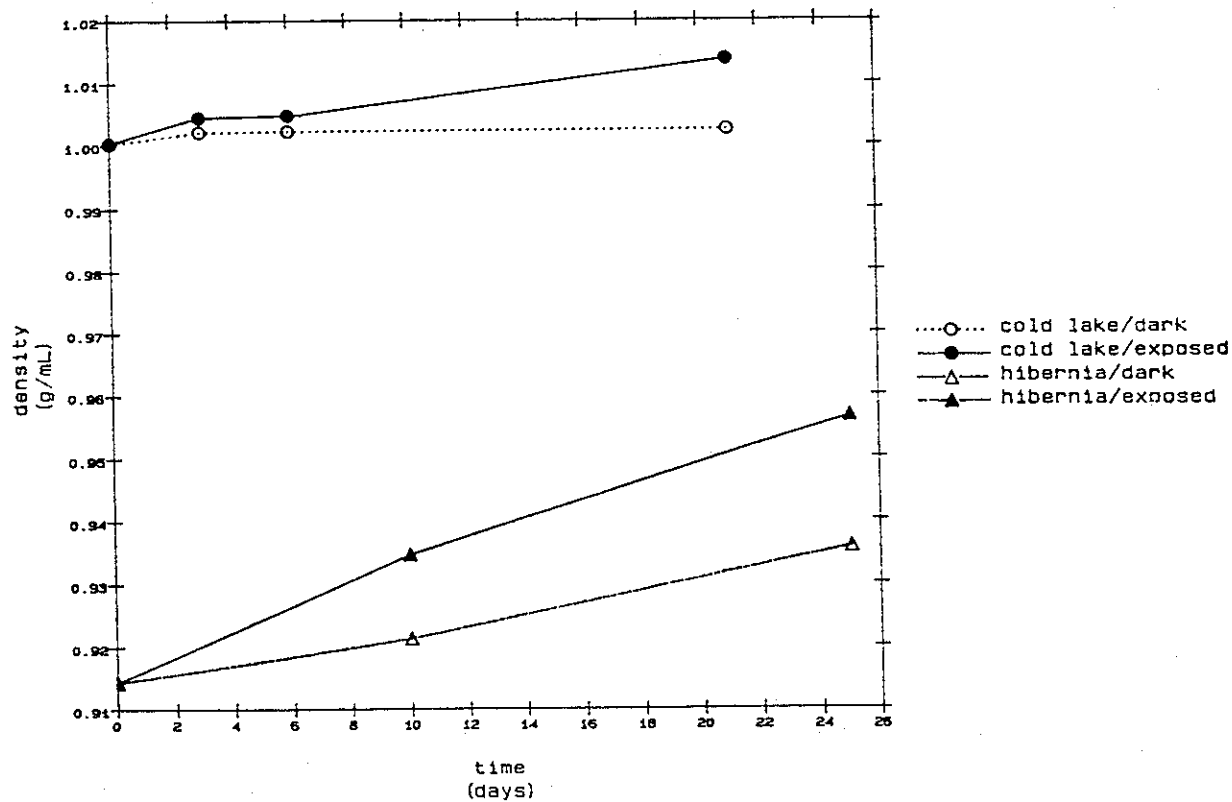


Figure 4: Density versus time



Figures 5 to 8 show the amount of oil in water measured by the Horiba Analyzer as a function of time. Similarly, the measured carbon content of water are presented in Figures 9 to 12. Since the water was filtered prior to performing these measurements, only dissolved molecules and sub-micron particles would be present in the water. In each case, the amount of material measured in the water was higher for irradiated samples. As noted in the observations (Table 1), water beneath irradiated oil became yellowish during exposure. The visual intensity of the yellow colour appeared to directly correlate with the measured carbon content. Previous studies have shown that photooxidation products from fuel oils are highly water soluble. (Poston et al. (1988); Herbes and Whitley (1983)) The higher oil content in the water under irradiated oil films suggests that the presence of photooxidized compounds leads to an increase in the amount of oil incorporated into water. The photooxidation products could possibly act as co-solvents which enhance the solubility of hydrocarbons in water. The photooxidation products probably also act as surfactants that stabilize sub-micron oil-in-water emulsions. GC/FID fingerprint tracings indicated that the hydrocarbon composition of water extracts were very similar to those of the surface oils; this would suggest that much of the oil measured in the water is in the form of oil-in-water emulsions.

Changes in the pH of water as a function of exposure time are presented in Figures 13 and 14. The pH of water beneath shielded oils exhibited no change with time and remained constant at a value of 8.5 ± 0.2 . The water beneath Diesel fuel oil and Bent Horn crude oil showed a sharp decrease in pH during irradiation. After 21 days, these water layers had pH readings of about 4. This clearly indicates that the photooxidation products formed by these oils are acidic in nature. The formation of organic acids during fuel oil irradiation had also been noted by Larson et al. (1979). Several studies have compared the toxicity of non-photolysed oil to photolysed oil, and they have shown that photolysis enhances toxicity. Our results indicate that if the species used in bioassays are sensitive to pH, the simple change in pH might be a factor. Under real marine spill conditions, it is unlikely that changes in pH would occur because of the buffer effect from surrounding water.

Although the results show that photolysis can significantly influence the amount of oil that enters the water column through dissolution and emulsification, a mass balance shows this quantity to be far less than 1% of the total mass of oil spilled. Figures 15 to 24 show a mass balance for each oil. Each graph illustrates what percent of the original mass of oil remained on the surface as a film (labelled 'SUR' on the graph); what percent of the oil evaporated ('AIR'); and what percent of the oil sank ('SED'). The quantity of oil that evaporated was calculated from the amounts measured in the other phases. At time zero (0 days), 100 % of the oil was on the surface. It should be again be mentioned that some of the oils were artificially evaporated prior to being used. This amount of pre-test evaporation is not included in these calculations. From these graphs, it is apparent that the importance of photolysis to the fate of an oil is dependent upon the oil itself. Exposure to solar radiation resulted in an increase in the amount of oil that "sedimented". Shielded oils had little sediment ($< 0.1\%$). Significant amounts of sedimented oil formed when California 11 and California 15 crude oils were irradiated; after 21 days of exposure, the percentage of oil that sedimented was 7 and 9 %, respectively.

Figure 5: Oil-in-water content versus time
Horiba Analyzer results

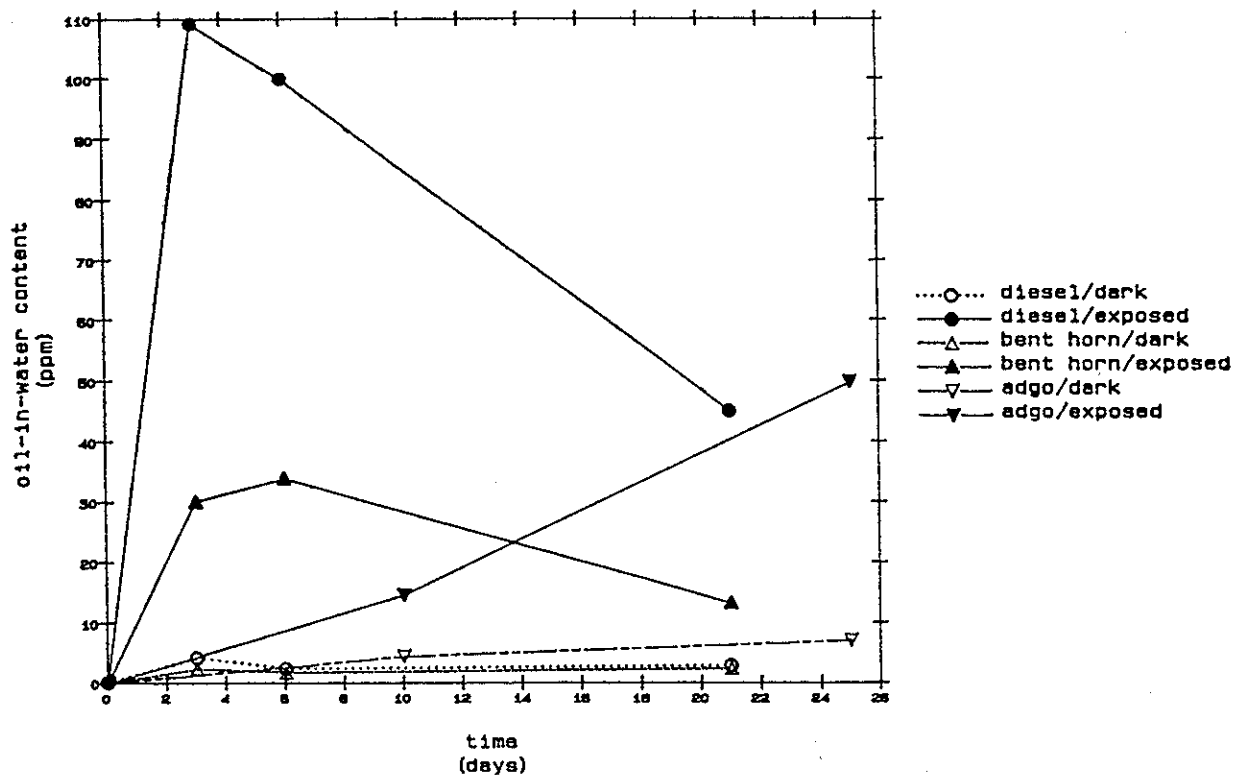


Figure 6: Oil-in-water content versus time
Horiba Analyzer results

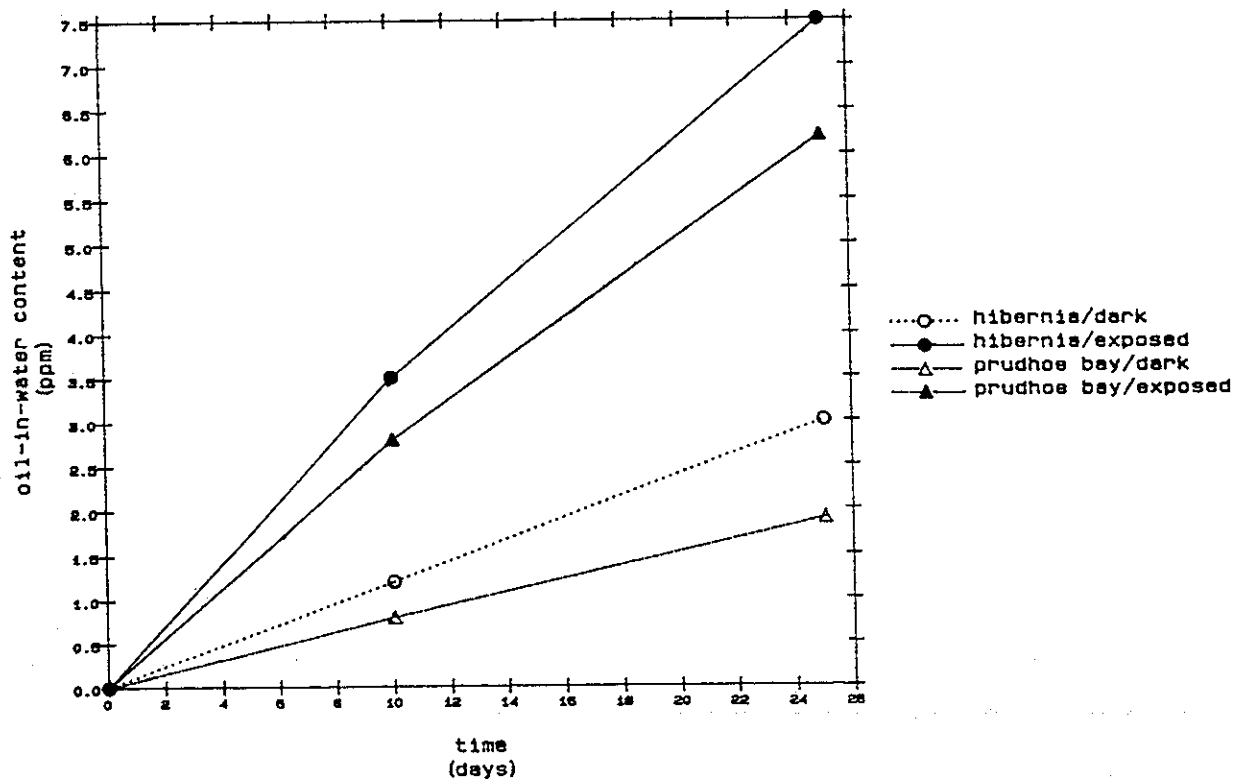


Figure 7: Oil-in-water content versus time
Horiba Analyzer results

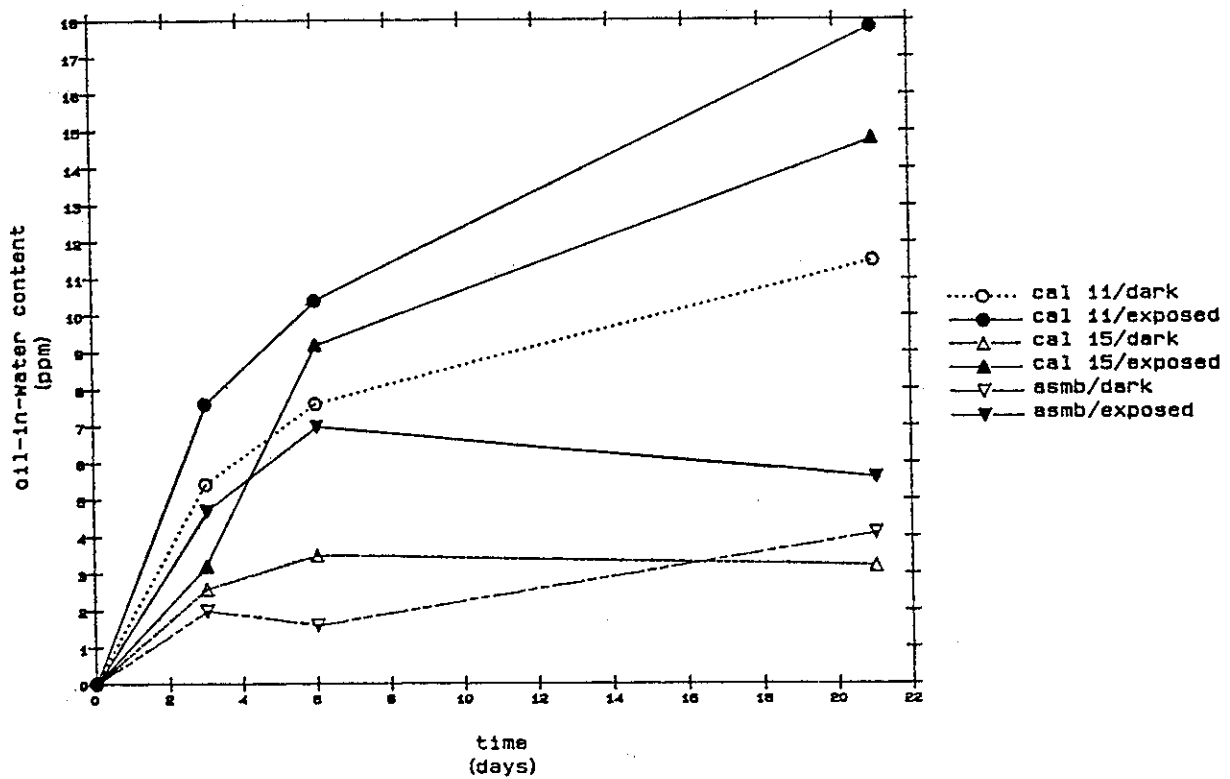


Figure 8: Oil-in-water content versus time
Horiba Analyzer results

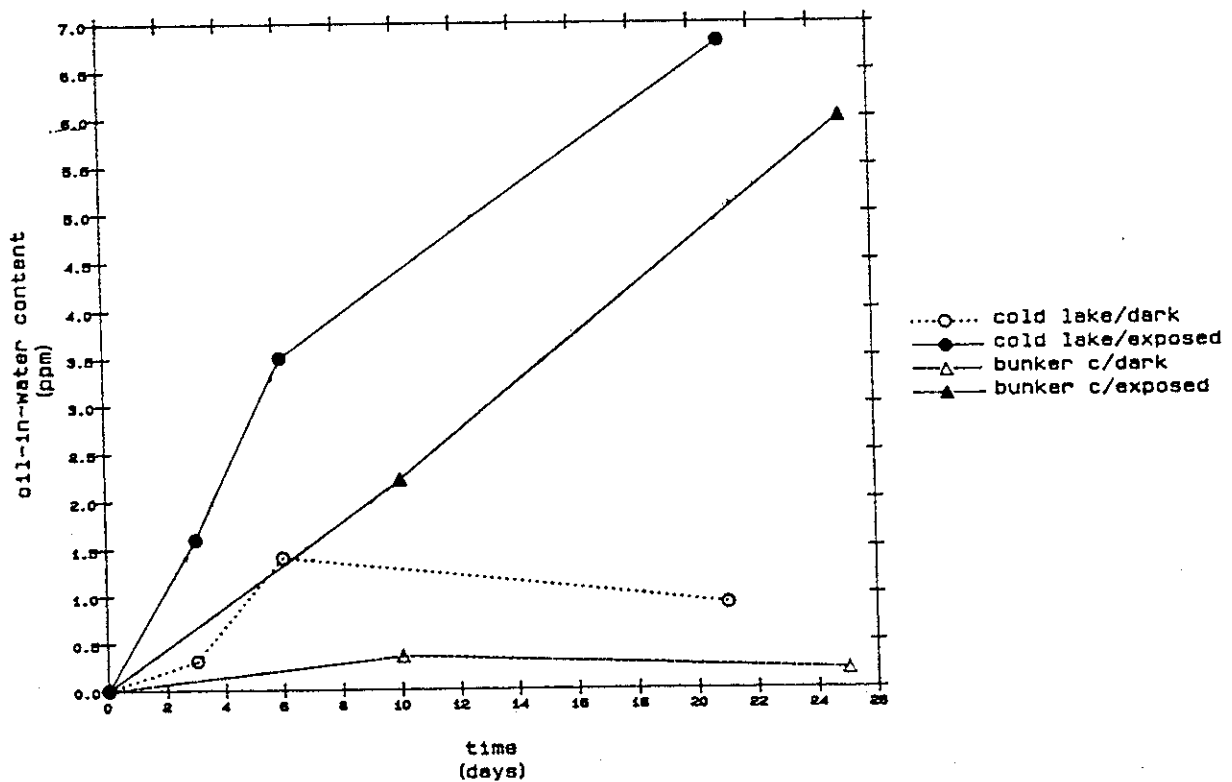


Figure 9: Carbon Content of Aqueous Phase

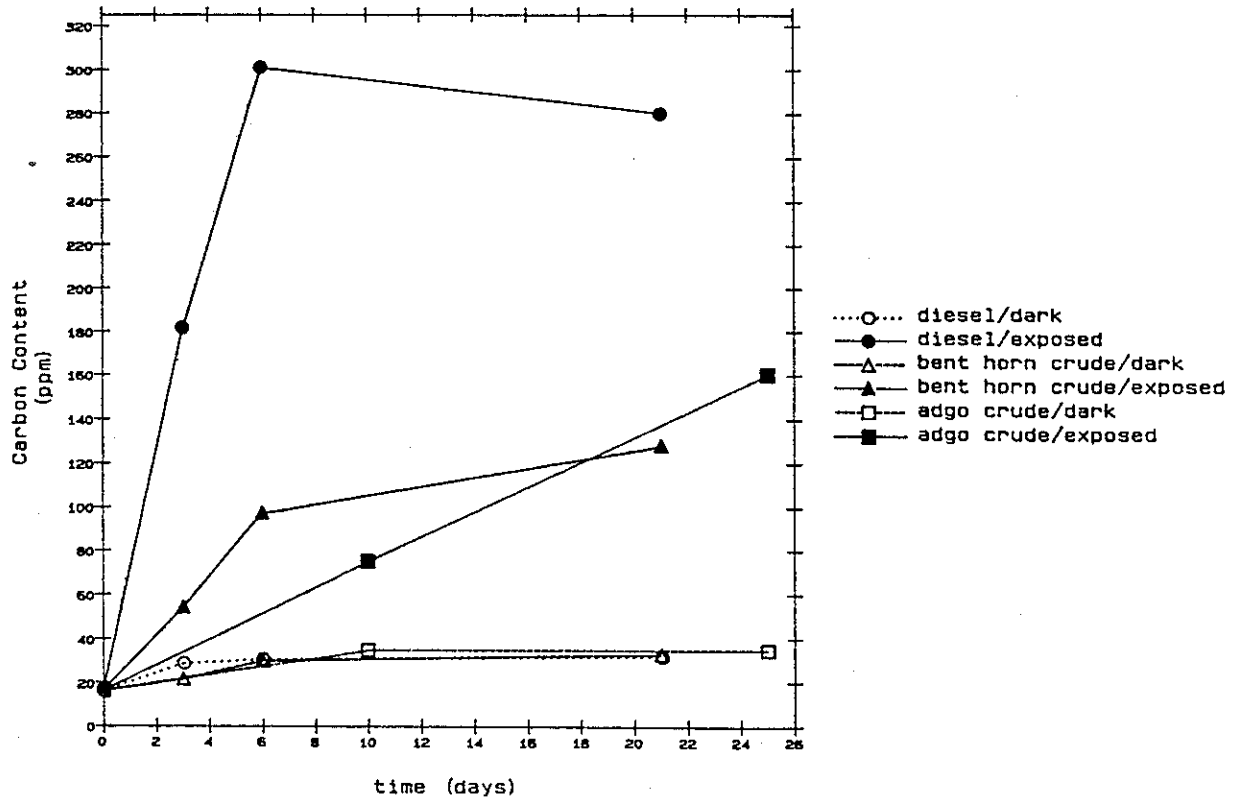


Figure 10: Carbon Content of Aqueous Phase

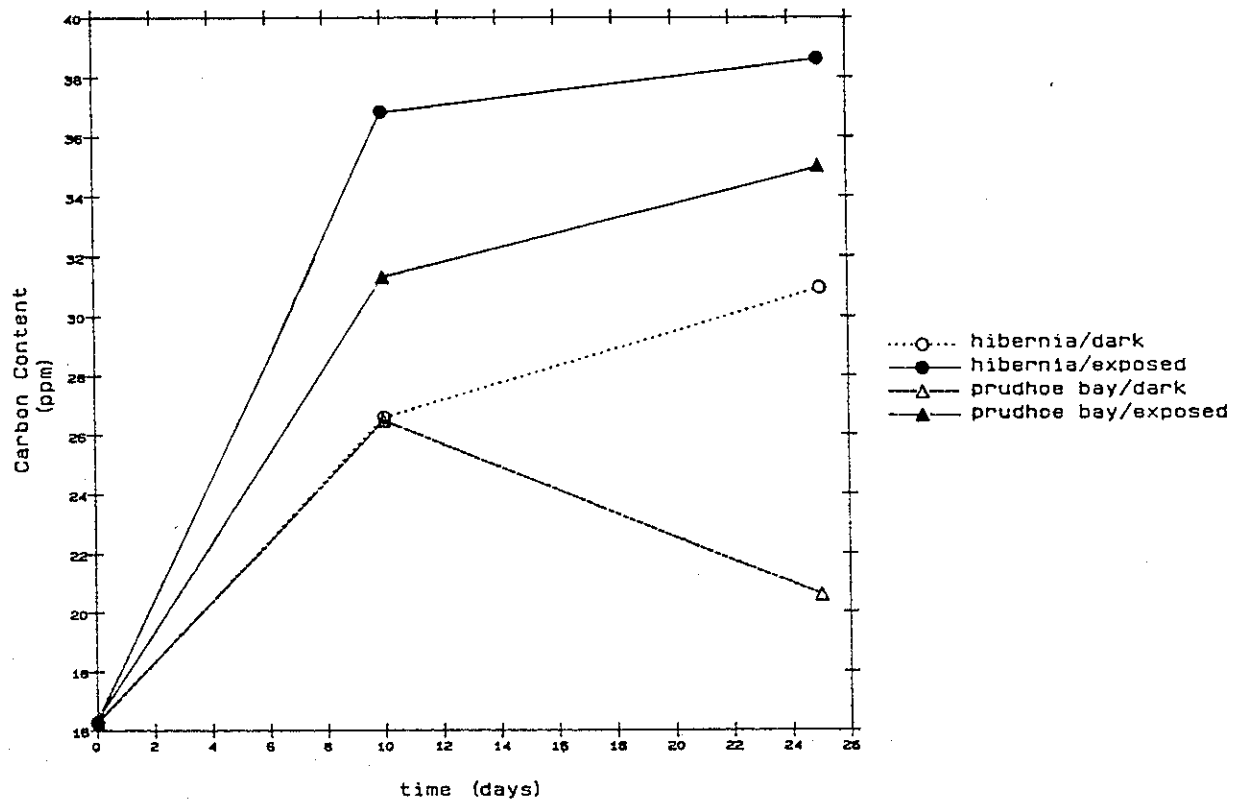


Figure 11: Carbon Content of Aqueous Phase

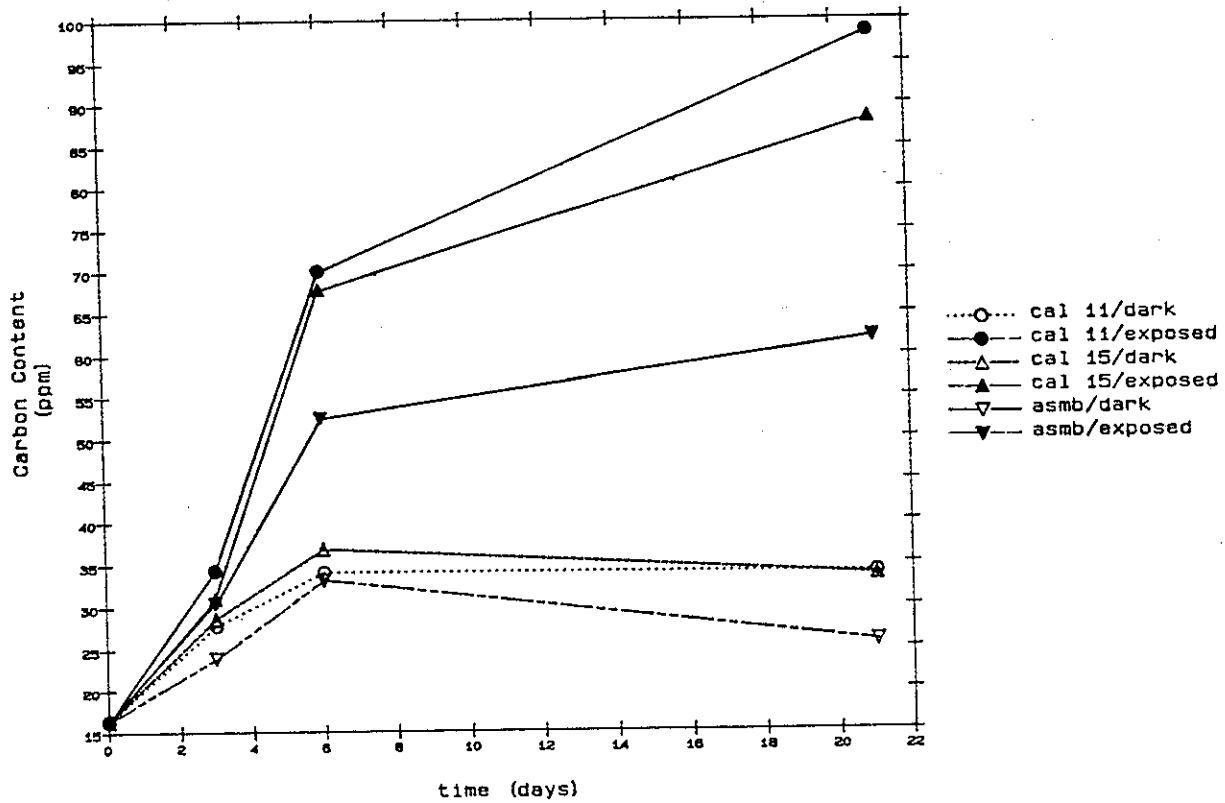
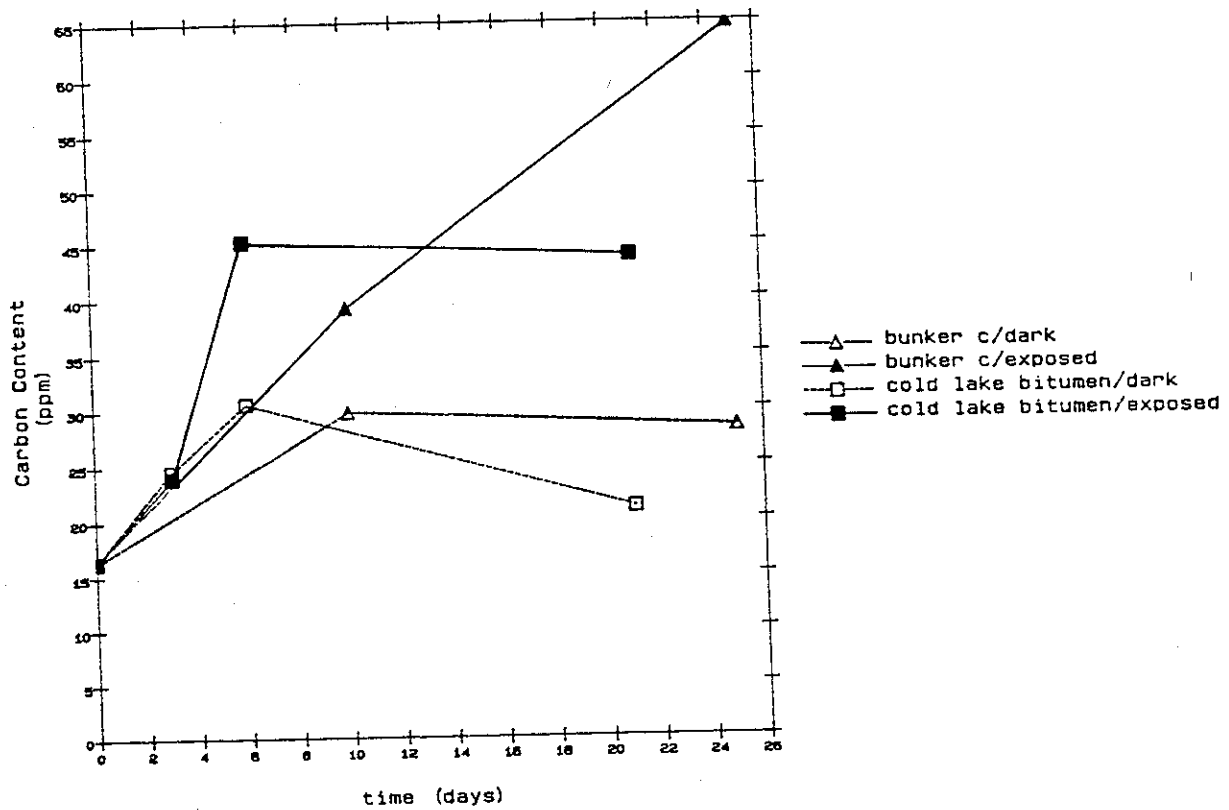


Figure 12: Carbon Content of Aqueous Phase



Mass Balances For Oils

Figure 13: pH of Aqueous Layer

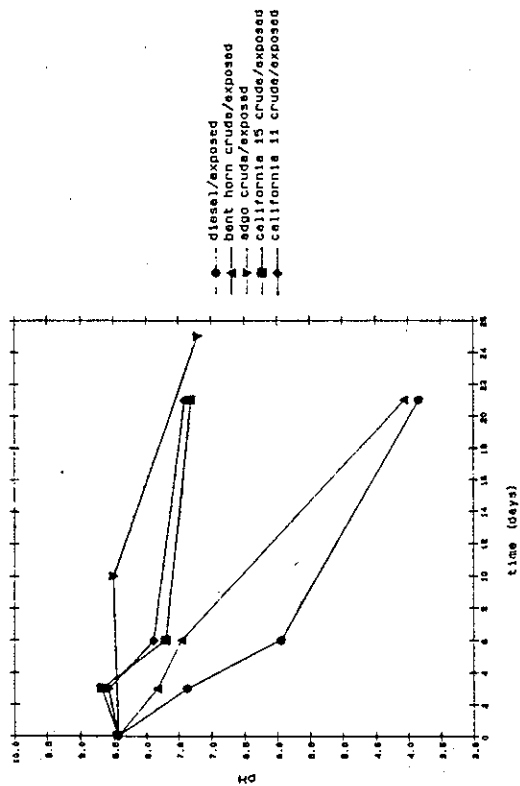


Figure 14: pH of Aqueous Layer

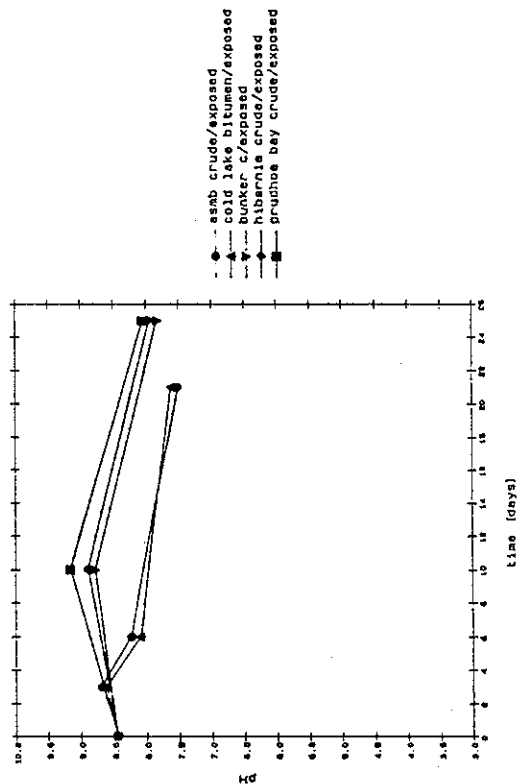


Figure 15:

diesel fuel oil

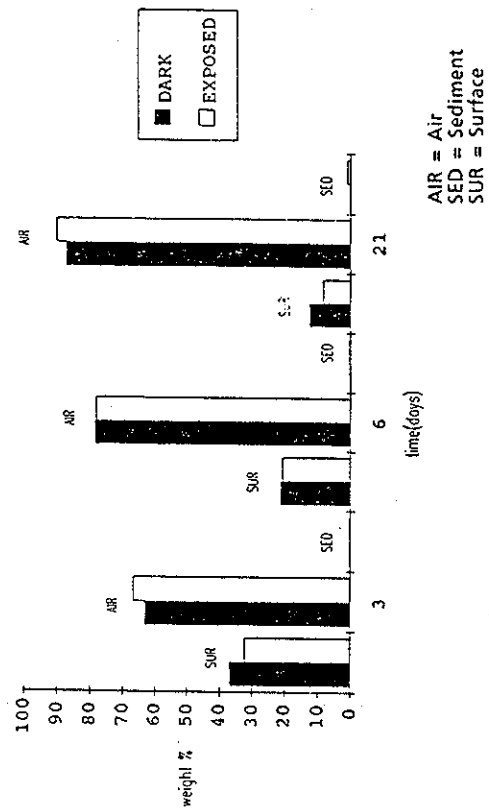


Figure 16:

bent horn crude

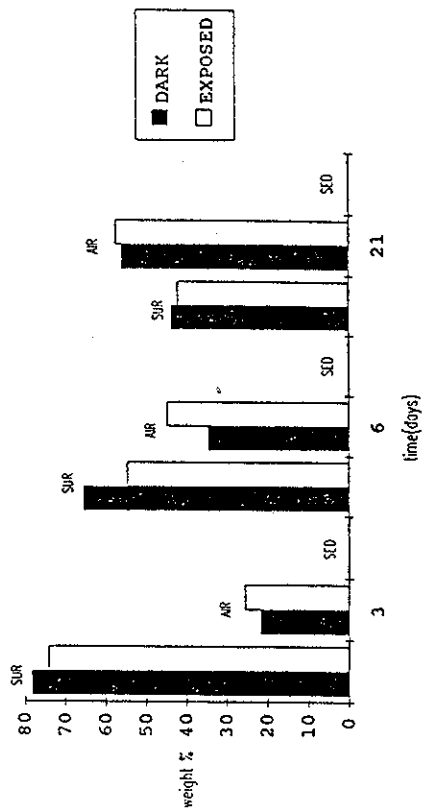


Figure 19: california 11 crude

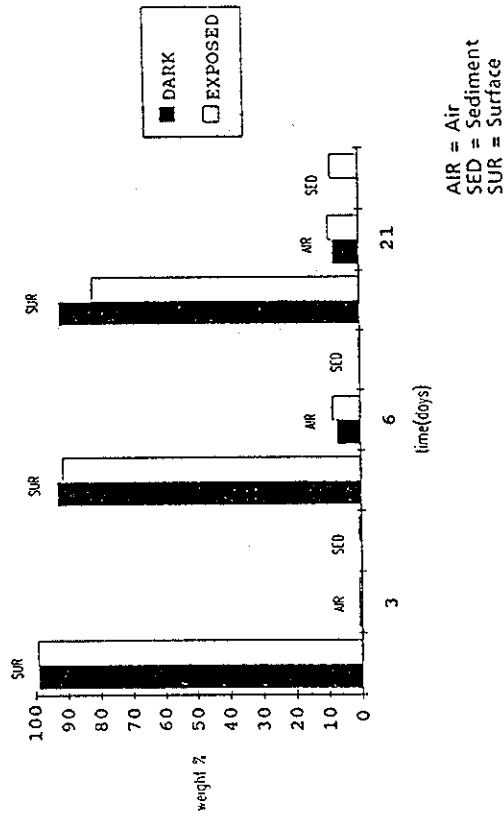


Figure 20: cold lake bitumen

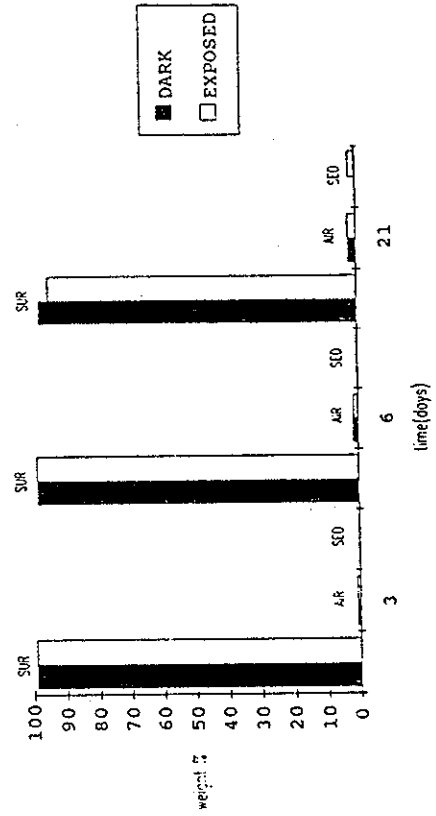


Figure 17: odgo crude

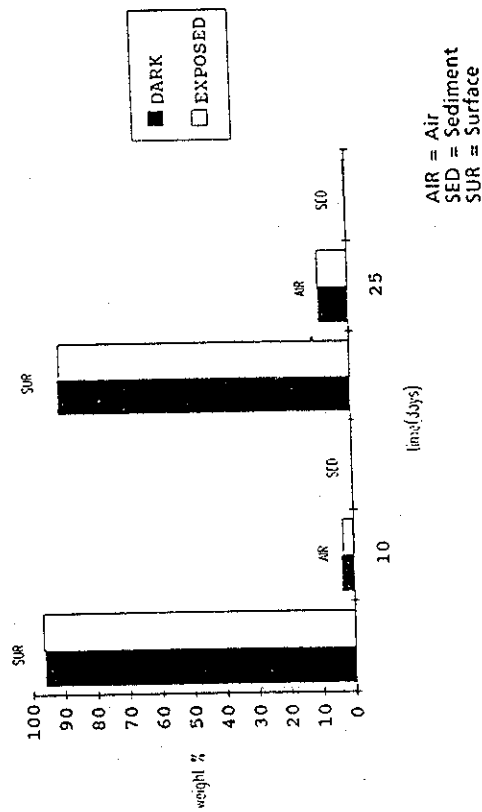


Figure 18: california 15 crude

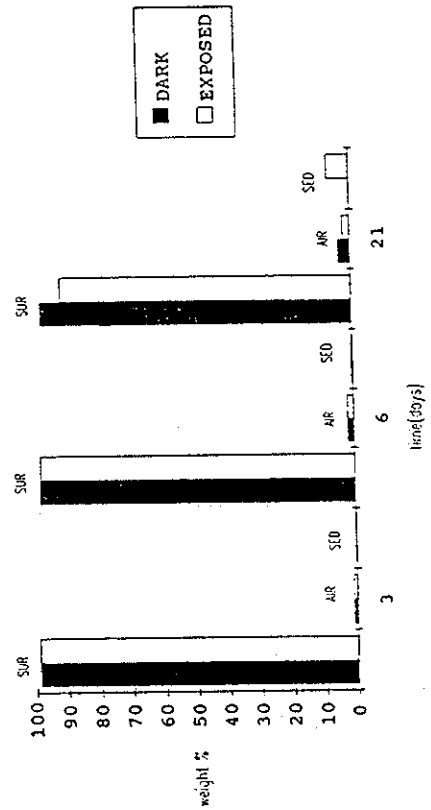
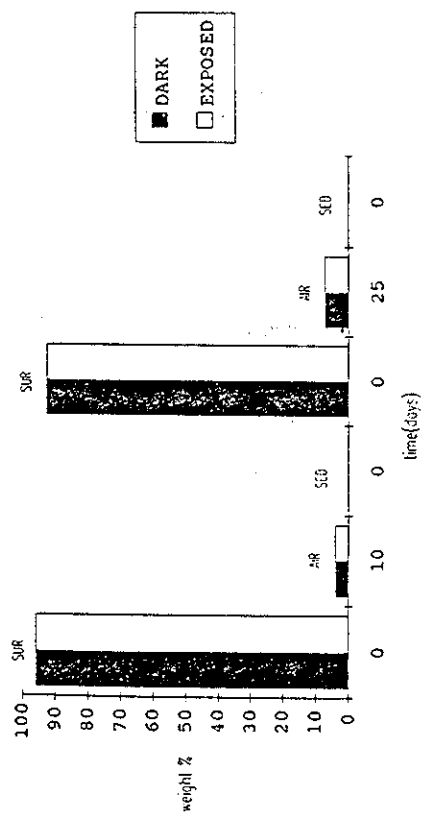


Figure 21: hibernia crude



AIR = Air
SED = Sediment
SUR = Surface

Figure 22: bunker c fuel oil

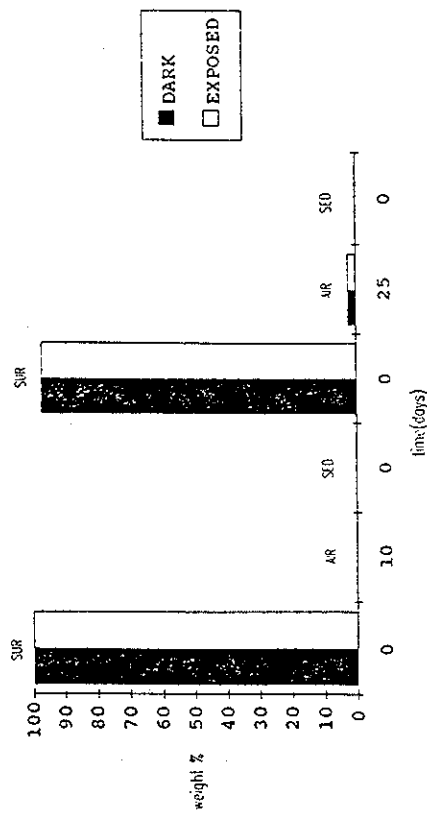
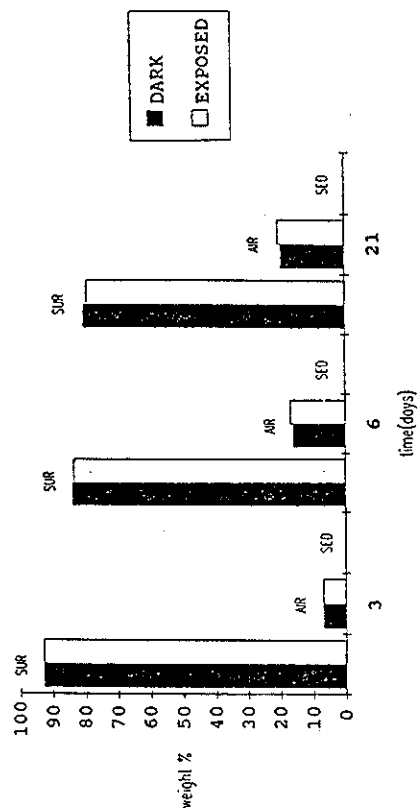
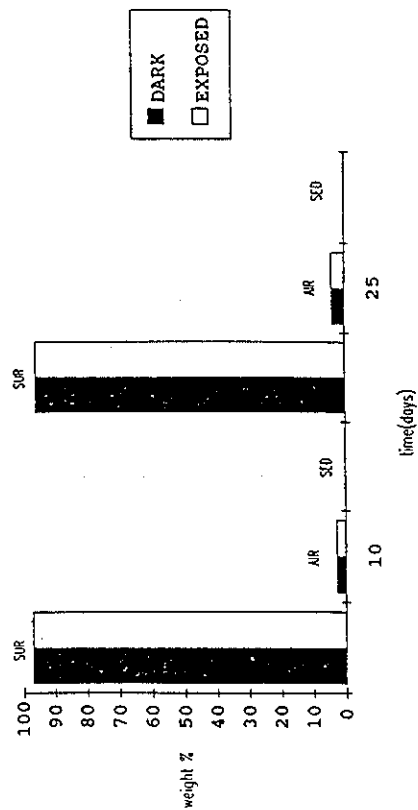


Figure 23: alberlo sweet mixed blend crude



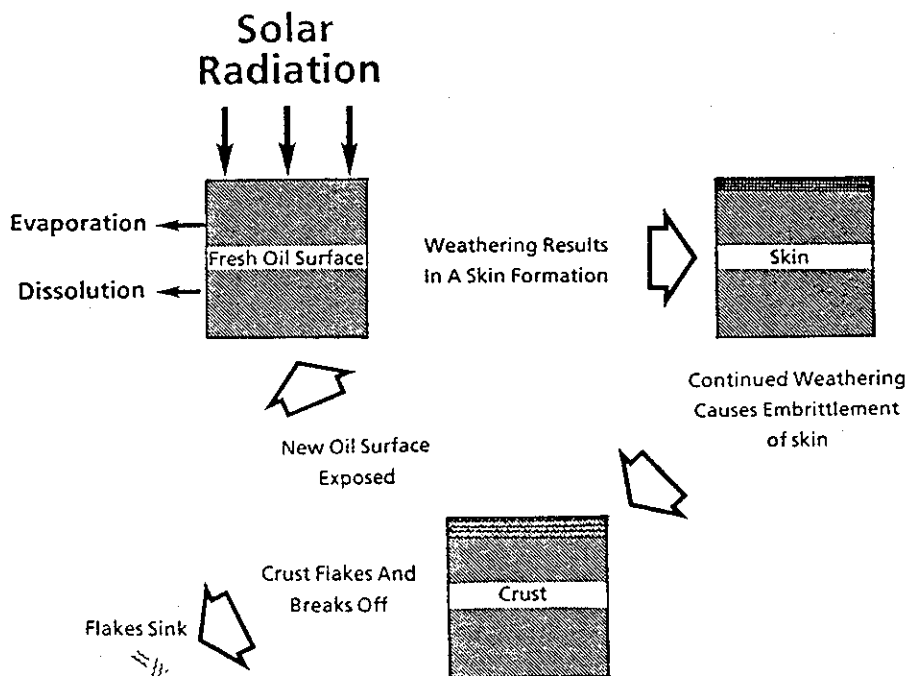
AIR = Air
SED = Sediment
SUR = Surface

Figure 24: prudhoe bay crude



From the physical changes observed in oils (Table 1) and from the results obtained, it is concluded that photo-induced reactions are responsible for the formation of materials which encrust oil. Figure 25 is a simple schematic diagram that illustrates how oil "crust" is formed. As oil weathers, a "skin" of dense material forms at the air-oil interface. This skin was observed to form on oils that were photolysed as well as on oils that were shielded. If this material is subjected to photolysis, it becomes embrittled thus forming a hardened crustal material. No crust was formed on oils kept in the dark. Further exposure causes the crustal material to form flakes which eventually break off and sink, thus exposing a new oil surface. The crusts observed in this study are similar in description to those found on tar balls by Morris et al. (1977).

Figure 25: CRUST FORMATION



CONCLUSIONS

The importance of photolysis as a weathering process will depend very much upon the type and composition of the oil. This study has identified several oils which are extremely sensitive to photooxidation, and it has demonstrated how photo-induced reactions can influence the fate and behaviour of these oils. Photolysis induced changes in physical properties and resulted in the formation of products that increased the amount of oil entering the water column.

ACKNOWLEDGEMENTS

This project was funded by the U.S. Minerals Management Service and the Environmental Emergencies Technology Division of Environment Canada. Mr. M. Fingas was the Scientific Authority. Dr. A. Bobra conducted the microbial examination of the samples.

REFERENCES

- Aberg, A., Pedersen, D. and Tjessem, K., "Factors Affecting the Extraction of Polar Environmental Constituents from Water", *Water Res.*, vol.19, no.2, pp.169-173, 1985.
- Aksnes, G. and Iversen, A., "Photooxidation of Diphenylmethane and 1,2,3,4-Tetrahydronaphthalene as Liquid Film on Water", *Chemosphere*, vol.12, no.3, pp.385-396, 1983.
- Barth, T., Tjessem, K. and Aaberg, A., "Fractionation of Polar Constituents in Environmental Samples Using the Lipophilic Dextran Gel Sephadex LH-20 and Sephasorb HP Ultrafine", *J. Chromat.* 214, pp.83-93, 1981.
- Daling P.S., "A Study of the Chemical Dispersibility of Fresh and Weathered Crude Oils", in proceedings of the eleventh Arctic and Marine Oil Spill Program technical seminar, pp.481-499, 1988.
- Daling, P.S. and Branvik, P.J., "A Study of the Formation and Stability of Water-in-oil Emulsions", in proceedings of the eleventh Arctic and Marine Oil Spill Program technical seminar, pp.153-170, 1988.
- Dulin, D. and Mill, T., "Development and Evaluation of Sunlight Actinometers", *Environ. Sci. Technol.* vol.16, no.11, pp.815-820, 1982.
- Fingas, M.F., "Dispersant Effectiveness at Sea: A Hypothesis to Explain Current Problems with Effectiveness", in proceedings of the eleventh Arctic and Marine Oil Spill Program technical seminar, pp.455-479, 1988.
- Freegarde, M., Hatchard, C.G. and Parker, C.A., "Oil Spilt at sea: Its Identification, Determination and Ultimate Fate", *C.A. Lab. Pract.*, 20-4, pp.35-40, 1971.
- Hansen, H.P., "Photochemical Degradation of Petroleum Hydrocarbons Surface Films on Seawater", *Marine Chemistry*, 3, pp.183-195, 1975.

- Herbes, S.E. and Whitley, T.A., "Characterization and Toxicity of Water-Soluble Photooxidants Produced During Irradiation of Coal Liquids by Sunlight", *Environ. Pollut. Ser. B*, no.6, pp.221-240, 1983.
- Larson, R.A., Bott, T.L., Hunt, L.L. and Rogermuser, K., "Photooxidation Products of a Fuel Oil and their Antimicrobial Activity", *Environ. Sci. Technol.*, vol.13, no.8, pp.965-969, 1979.
- Lee, S.C., Mackay, D., Bonville, F., Joner, E. and Shiu, W.Y., "A Study of the Long-term Weathering of Submerged and Overwashed Oil", report prepared for Environmental Emergencies Technology Division, Environment Canada, 1989.
- Lichtenthaler, R.G., Hoag, W.R. and Mill, T., "Photooxidation of Probe Compounds Sensitized by Crude Oils in Toluene and as an Oil Film on Water", *Environ. Sci. Technol.* 23, pp.39-45, 1989.
- Morris, B.F., Butler, J.N., Sleeter, T.D. and Caldwell, J., "Particle Hydrocarbon Material in Ocean Waters", *Rapp.P.-v. Reun. Cons. Int. Explr. Mer.* 171:107-116, 1977.
- Patel, J.R., Overton, E.B. and Laseter, J.L., "Environmental Photooxidation of Dibenzothiophenes Following the Amoco Cadiz Oil Spill", *Chemosphere*, no.8, pp.557-561, 1979.
- Payne, J.R. and Phillips, C.R., "Critical Review - Photochemistry of Petroleum in Water", *Environ. Sci. Technol.*, vol.19, no.7, pp.569-579, 1985.
- Pengerud, B., Thingstad, F., Tjessem, K. and Aaberg, A., "Photo-induced Toxicity of North Sea Crude Oils Toward Bacterial Activity", *Mar. Poll. Bull.*, vol.15, no.4, pp.142-146, 1984.
- Poston, T.M., Bean, R.G., Kalkwarf, D.R., Thomas, B.L., Clark, M.L. and Killard, D.R., "Photooxidation Products of Smoke Generator Fuel (SGF) No.2 Fog Oil and Toxicity to *Hallela Azteca*", *Environ. Toxicol. Chem.*, vol.7, pp.753-762, 1988.
- Sydnos, L.K., Burkow, I.C., Stene, A. and Lonning, S., "On the Formation of Short-lived, Toxic, water-soluble Compounds During Illumination of Crude Oil on Seawater", *Marine Environ. Res.* 16, pp.115-126, 1985.
- Sydnos, L.K., Hansen, S. and Burkow, I.C., "Factors Affecting Photooxidation of Oil Constituents in the Marine Environment. I. Photochemical Transformations of Dimethylnaphthalenes in an aqueous Environment in the Presence and Absence of Oil", *Chemosphere*, vol.14, no.8, pp.1043-1055, 1985.
- Sydnos, L.K., Hemmingsen, T.H., Solvi, S., Hansen, Falk-Petersen, I, Lonning, S., and Ostgaard, K., "Seasonal Variations in Weathering and Toxicity of crude Oil on Seawater under Arctic Conditions", *Environ. Sci. Technol.*, vol.19, no.11, pp.1076-1081, 1985.
- Tjessem, K., Kobberstad, O. and Aaberg, A., "Photochemical Transformation and Degradation of Petroleum Residues in the Marine Environment / Photochemically Induced Interactions in Ekofisk Crude Oil", *Chemosphere*, vol.12, no.11/12, pp.1373-1406, 1983.